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Micro-scale Lead and Minerals Distribution in Shooting Range Soils

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Beamline(s): X26A

Introduction: The environmental impact of lead contamination of soils by shotgun bullets in the vicinity of shooting ranges is investigated. Previous observations indicate that, depending on the chemistry of their environment, the Pb bullets can develop corrosion coatings within a few years, consisting of mineral phases, which can have a relatively high solubility at commonly slightly acidic soil pH. On the other hand, aqueous Pb is generally tightly bound by soil organic matter and clay minerals. Therefore, little is still known on the development of high subsoil lead concentration under topsoil rich in shot bullets.

Methods and Materials: Undisturbed soil samples were collected in the profile of a shooting range stop butt where the soil is calcareous and low in organic matter content. Samples were embedded in resin to prepare polished thin sections. Then, detailed mapping of these thin sections were collected on X26A with a beam size of 15 μm . Micro-XRF was used to investigate the spatial distribution of lead (and other trace metals provided by the bullets: Cu, Zn, Sb, Ni), μ -XANES to determine the speciation and oxidation state of lead and μ -XRD to evidence the possible crystalline phases of lead and the other trace metals and to determine the minerals on which they are sorbed.

Results: We focused on bullets and their immediate surroundings. Because of the impact, the bullet cores in the soil are separate from the mantle. Consequently, we investigated two areas of special interest: the oxidized bullet core (mainly composed by Pb and Sb) and corrosion area and the oxidized bullet mantle (rich in Fe, Ni and Cu) and its immediate surroundings.

In the mantle corrosion area, the XRF data clearly evidence the migration of metals into the soil, which is less important for Cu and Ni. These two elements seem remain in the metallic form longer than iron. Since lead concentration was low enough, XRD patterns were collected. The observed diffraction peaks are variable depending on distance to the mantle. However, the evaluation of XRD data has not yet been completed. In the bullet core and corrosion area, XRF elemental mapping clearly shows that the bullet cores contain only Pb and Sb. The fate of Sb is difficult to follow in this calcium rich soil because of the Sb-L and Ca-K lines overlapping. Pb migrates into the immediate surrounding soil and, beyond a distance close to one millimeter, its concentration decreasing rapidly. The XRF spectra also show the presence of iron, nickel, zinc and copper in soil. XANES spectra collected at the Pb-L_{III} edge in the bullet core confirms that lead is in the 0 valence state. In the corrosion area and in the near surrounding soil, the position of the edge reveals that lead is divalent. The spectra analysis with a linear combination of reference spectra shows the succession of lead secondary mineral phases. Close to the bullet (until 100 μm) litharge is formed. Then hydrocerussite and cerussite appear (until 1 mm to the bullet). The final oxidation product, cationic lead, migrates into the soil.